

Final Report for “**Growth Control of Carbon Nanowalls**”

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Research Theme: Growth Control of Carbon Nanowalls

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Brief Overview of the Investigation

➤ Problem Statement:

For the application of carbon nanowalls to the electronic devices, it is necessary to clarify their growth mechanism and to attain their growth control including morphology control, position-controlled growth, and control of their electrical property.

➤ Program Objectives:

- Elucidation of the formation mechanism of carbon nanowalls at the early stage of growth
- Development of methods for position-controlled growth of carbon nanowalls

➤ Approach:

Realization of growth control of carbon nanowalls by (1) selective supply of specific species using the multi-beam CVD and (2) surface reaction control

➤ Research Results:

- Carbon nanowalls were successfully grown by the simultaneous irradiation of fluorocarbon radicals, hydrogen atoms, and Ar ions and it was confirmed that the ion bombardment is crucial for the nucleation of carbon nanowalls.
- Carbon nanowalls were grown area-selectively on the substrate through using patterned catalyst or with the help of deep trenches. The nucleation rate of carbon nanowalls depended on the class and forms of substrate materials. The growth of carbon nanowalls was enhanced on the Ti thin layer. Similar enhancement was observed on the thin layer or nanoparticles of Co, Pt and Fe.

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14. ABSTRACT Growth mechanisms of carbon nanowalls for electronic device applications were explored. Properties investigated include morphology control, position-controlled growth, and control of their electrical property. During the course of this work, carbon nanowalls were successfully grown by the simultaneous irradiation of fluorocarbon radicals, hydrogen atoms, and Ar ions and it was confirmed that the ion bombardment is crucial for the nucleation of carbon nanowalls. Additionally, carbon nanowalls were grown area-selectively on the substrate through using patterned catalyst or with the help of deep trenches. The nucleation rate of carbon nanowalls depended on the class and forms of substrate materials. The growth of carbon nanowalls was enhanced on the Ti thin layer. Similar enhancement was observed on the thin layer or nanoparticles of Co, Pt and Fe.					
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1. Background

Two-dimensional (2D) graphene sheets, which range from a single layer to stacks of a few layers, have attracted great interest for use in next-generation electronic devices (Nature Mater. **6**, (2007) 183). Few-layer graphene sheets have been reported to have high mobility of 10,000–15,000 cm²/Vs and a band gap of 0.26 eV. However, the primary method for isolating graphene, i.e., micromechanical cleavage of highly orientated pyrolytic graphite bulk, cannot be easily scaled up for large-scale applications.

Recently, several reports have been published on the growth of carbon nanowalls, self-organized graphite nanostructures comprised of planar graphene layers. Carbon nanowalls can be described as graphite sheet nanostructures with edges that are composed of stacks of planar graphene sheets standing almost vertically on the substrate. The sheets form a self-supported network of wall structures with thicknesses ranging from a few nanometers to a few tens of nanometers, and with a high aspect ratio (Fig. 1). Because of the unique structure of carbon nanowalls with high aspect ratio and high surface-to-volume ratio, carbon nanowalls can be potentially used as electron field emitters and as catalyst support materials. Furthermore, since carbon nanowalls essentially consist of graphene sheets, they are expected to have high mobility and large sustainable current density. Therefore, carbon nanowalls are considered to be one of the most promising carbon materials used for nanoscale electronic devices. However, in order to fully exploit the potential of graphene and to develop next-generation electronic devices, further investigations must be performed to enable control over the structure and electronic properties of carbon nanowalls, as well as to establish a carbon nanowall fabrication system with high productivity.

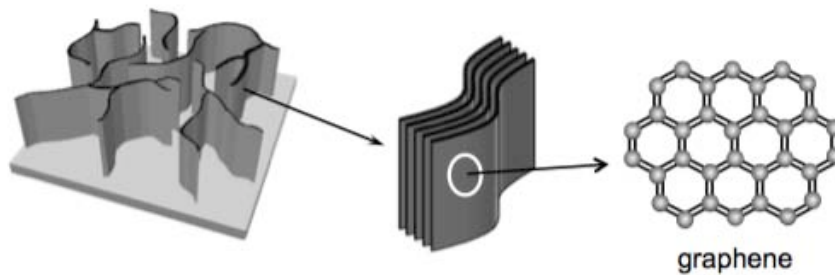


Fig. 1 Schematic illustration of carbon nanowalls

This research aims to control the growth of carbon nanowalls and to optimize their structure and electrical properties toward the use for nanoscale electronic devices. To achieve this, it will be necessary to:

- (1) Investigate the nucleation and growth mechanism of carbon nanowalls and develop methods for the control of carbon nanowall growth.
- (2) Investigate methods for the fabrication of isolated carbon nanowalls (graphene sheet).
- (3) Evaluate the electronic properties of isolated carbon nanowalls and control them.

2. Method of Investigation

Significant interest exists in clarifying the nucleation mechanism of carbon nanowalls and controlling the growth of carbon nanowalls for obtaining the isolated, self-sustaining carbon nanowall (graphene sheet) with good crystallinity. To achieve this, the experiments were carried out by two approaches as described below.

First phase of this research focused on the investigation of the nucleation of carbon

nanowalls by using the multi-beams of carbon source, hydrogen and ions in order to clarify the growth mechanism of carbon nanowalls at the very early stage and to develop methods for position-controlled growth of carbon nanowalls.

Second phase explored the alternative approaches to achieve the growth control of carbon nanowalls based on the surface reaction control e.g., by using the patterned substrates and nano-dot array of metal catalysts for obtaining aligned carbon nanowalls with controlled intervals and isolated monolithic carbon nanowall.

3. Research results

3.1 Nucleation Mechanism of Carbon Nanowall Growth Under Ion Irradiation

In the case of carbon nanowall growth employing C_2F_6/H_2 system, CF_3 radicals and H atoms are considered to be important species. In addition to the dominant radicals, however, at the onset of carbon nanowall nucleation in the initial growth stage, ionic species may contribute to the nucleation of carbon nanowalls. The ionic species bombard the substrate or growing surface, resulting in the enhancement of deposition, etching, or surface modification of growing surface physically and chemically. To elucidate the role of ionic species in the nucleation of carbon nanowalls, multi-beam chemical vapor deposition (CVD) system is constructed, where H and fluorocarbon radical sources and an ion source are installed and the heated substrate is exposed to specific radicals and ions at the same time in a controlled manner.

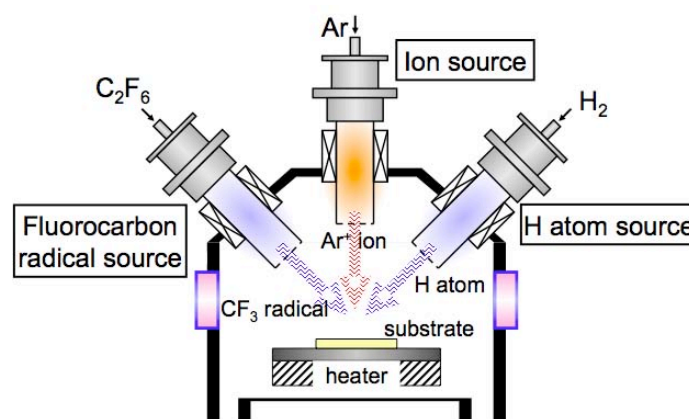


Fig. 2 Schematic illustration of multi-beam CVD system equipped with two radical sources and an ion source

Carbon nanowalls were synthesized by the simultaneous irradiation of H and fluorocarbon radicals and ions. Figure 2 shows a schematic of multi-beam CVD system equipped with two radical sources and an ion source. Two identical radical sources for H and fluorocarbon radicals, which were mounted on both sides of the chamber, consisted of radio frequency (RF: 13.56 MHz) inductively coupled plasma (ICP) and two grounded metal meshes in the head to retard ejection of electrons and ions. C_2F_6 and H_2 gases were introduced into each source separately. The dominant radical from the dissociation of C_2F_6 gas was evaluated to be CF_3 . The radicals generated in each source irradiated the heated Si substrate at an angle of 30° from the horizontal plane. On the other hand, the ion source consisting of RF (13.56 MHz) ICP was mounted on the top of the chamber. The plasma potential in the ICP for ion source was changed in the range of 0–300 V by applying DC voltage. A metal mesh connecting to the ground was installed in the head of the ion source. In this experiment, Ar gas was used for the ion source. Generated Ar ions

were accelerated between the ICP and the metal mesh on the head, and they irradiated vertically the substrate with an energy ranging from 0 to 300 eV. The energetic Ar ions dominantly donate physical momentum effects, resulting in the enhancement of chemical reaction under the H and fluorocarbon radical irradiations. Thereby, we focused on the effects of Ar ion irradiation with controlled energy and flux on the formation of carbon nanowalls under simultaneous irradiation of H radicals and fluorocarbon radicals.

Growth experiment was carried out under simultaneous irradiations of H and fluorocarbon radicals and Ar ions. The flow rates of H₂, C₂F₆, and Ar were 6, 10, and 5 sccm, respectively, and the total gas pressure was 2.5 Pa. The RF powers for both radical sources and ion source were 200 and 300 W, respectively, and the substrate temperature was kept at approximately 580 °C. At this condition, CF₃ radical density around the substrate was estimated to be on the order of 10¹¹ cm⁻³ by appearance mass spectrometry, while the H radical density measured by vacuum ultraviolet absorption spectroscopy was 4 × 10¹¹ cm⁻³. The flux and energy of Ar ions irradiating the heated Si substrate were kept at 3.8 mA/cm² and 200 eV, respectively.

Figures 3(a) and 3(b) show tilted SEM images of the deposits formed for 15 and 50 min, respectively. As shown in Fig. 2(a), several nanoislands, approximately 10 nm in size and 5 nm in height, were formed on the substrate in 15 min. On the other hand, carbon nanowalls were actually formed after the growth for 50 min as shown in Fig. 2(b). Thus, it is confirmed that carbon nanowalls were grown by multi-beam CVD with the simultaneous irradiation of H and fluorocarbon radicals and Ar ions.

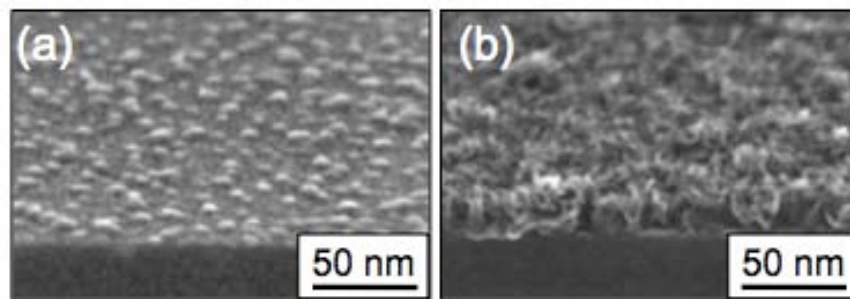


Fig. 3 Tilted-view SEM images of deposits formed for (a) 15 and (b) 50 min by multi-beam CVD system equipped with two radical sources and an ion source.

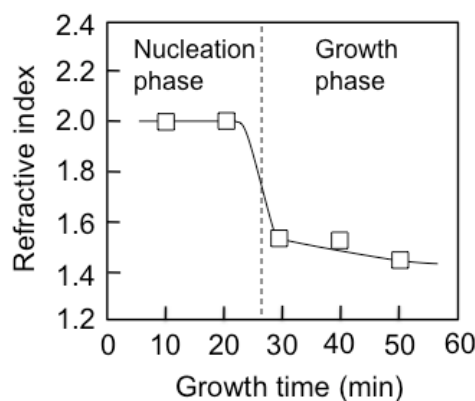


Fig. 4 Time behavior of refractive index of deposits formed by multi-beam CVD system, which was obtained from *in situ* ellipsometric analysis by considering structural factors of the film.

Figure 4 shows a time behavior of refractive index of deposits formed by multi-beam CVD system, which was obtained from *in situ* ellipsometric analysis by considering structural factors of the film. As shown in Fig. 4, the refractive index of deposits was almost constant at approximately 2.0 up to 20 min; this value was found to be similar to that of amorphous carbon film. In contrast, after 20-min growth the refractive index of deposits decreased abruptly and then became constant at approximately 1.4 with further increase of growth time. The result in Fig. 4 indicates that the structural phase transition occurs from “nucleation phase” to “growth phase” at the early stage of carbon nanowall growth. The nucleation phase consisted of the formation stage of nanoislands of amorphous carbon on the plain substrate. The SEM image in Fig. 3(a) represents the typical morphology of deposits in the nucleation phase. After a certain duration of nucleation, vertically standing nanographene started to grow on the nanoislands of amorphous carbon, resulting in the transition to growth phase.

Without Ar ion irradiation, in the case of deposition by multi-beam CVD, carbon nanowalls were not grown for at least 50 min. In order to investigate the effects of Ar ion irradiation on the nucleation and growth of carbon nanowalls separately, growth process was divided into two steps, the first step for nucleation phase (0–15 min) and the second step for growth phase (15–50 min), and growth experiment was carried out with and without Ar ion irradiation for each step. To investigate the effect of ion irradiation in the nucleation phase, growth experiment was conducted by multi-beam CVD for 15 min with and without the Ar ion irradiation. In this case, the flux and energy of Ar ions irradiating the heated Si substrate were kept at 1.8 mA/cm^2 and 200 eV, respectively. Furthermore, the flow rates of H_2 , C_2F_6 , and Ar were 6, 5, and 10 sccm, respectively, and the total gas pressure was 2.0 Pa; in order to prevent the phase transition from nucleation to growth mode in this period, the C_2F_6 flow rate was reduced, the Ar flow rate was increased, and the Ar ion flux was reduced, compared with the condition used for the previous growth experiment conducted in single step shown in Figs. 3 and 4. In the case of deposition with Ar ion irradiation, nanoislands were formed on the substrate for short period of 15 min, and their sizes and refractive index were found to be similar to those of the nanoislands shown in Fig. 3(a). In contrast, in the case of deposition without Ar ion irradiation, no nanoislands were formed, indicating that the ion irradiation is crucial for the nucleation of carbon nanowalls. As a result, we regard the 15-min deposition with Ar ion irradiation under the above-mentioned condition as a valid nucleation process.

Next, the above-mentioned 15-min nucleation process with Ar ion irradiation was followed successively by the second step of growth phase for 35 min at various Ar ion fluxes and energies under the previous condition for the flow rates of H_2 , C_2F_6 , and Ar. The structures of deposits formed by multi-beam CVD with simultaneous irradiation of H and fluorocarbon radicals and Ar ions at various Ar ion fluxes and energies in the growth phase are plotted in Fig. 5. White and gray pillars in Fig. 5 represent the formation of carbon nanowall (CNW) and amorphous carbon films, respectively, and the height of pillars corresponds to the relative height of deposits (or film thickness). As can be seen in Fig. 5, carbon nanowalls could be grown in the Ar ion flux region of approximately $3\text{--}4 \text{ mA/cm}^2$ and energy region of approximately 150–250 eV, which is indicated by oval marked “CNW.” For the growth of carbon nanowalls, a certain amount of Ar ion flux (more than 2.5 mA/cm^2 in this case) was required. On the other hand, excess ion flux resulted in the formation of amorphous carbon film. In contrast, with increasing Ar ion energy more than 250 eV, films were not formed on the substrate. These results indicated that Ar ion irradiation enhanced surface reaction in the growth phase including the adsorption of CF_3 radicals on the nucleated sites and the subtractive reaction of fluorine with H atoms,

whereas too much Ar ion irradiation prevented the formation of carbon nanowalls.

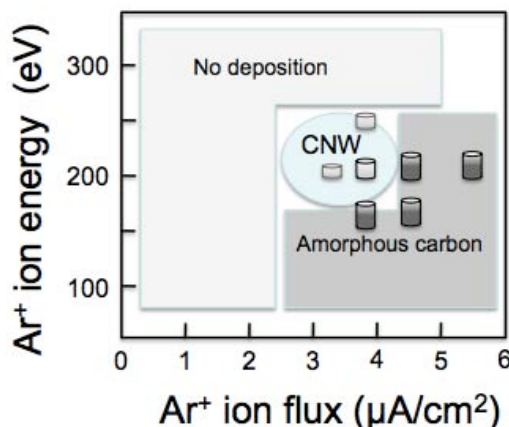


Fig. 5 A summary of structures of deposits formed by multi-beam CVD with simultaneous irradiation of H and fluorocarbon radicals and Ar ions at various Ar ion fluxes and energies in the growth phase. White and gray pillars represent the formation of carbon nanowall (CNW) and amorphous carbon films, respectively, and the height of pillars corresponds to the relative height of deposits (or film thickness)

The Ar ion irradiation would induce the formation of dangling bonds on the growing surface, resulting in the formation of nucleation sites. Furthermore, the Ar ion irradiation would also enhance the adsorption of CF_x radicals on the surface due to the fact that the sticking coefficient of CF_3 increases by the ion bombardment, although it is relatively low without the ion bombardment. However, Ar ions with low energy cannot induce such nucleation, while Ar ions with very high energy inhibit the growth of carbon nanowalls due to etching effects. In contrast, when the Ar ion flux is too large, the deposition rate of undesirable carbons also becomes higher, and then aggregation of nanographenes with random orientation or amorphous carbon films would be formed. Therefore, vertical growth of graphene sheets to form carbon nanowalls requires Ar ion irradiation with appropriate energy and flux.

3.2 Area-Selective Growth of Carbon Nanowalls

Unlike the carbon nanotube growth, carbon nanowalls can be grown on a variety of substrates without the use of catalyst, and the distribution of the nanowalls is relatively uniform over the whole substrate surface. At the same time, it is difficult to realize area-selective growth of carbon nanowalls. Meanwhile, the morphology and growth rate would occasionally depend on the substrate materials. For example, in the case of atmospheric pressure plasma-enhanced CVD, carbon nanowalls were successfully grown on the Ti-coated Si substrate, but not on the Si, for 30 min. These facts would give us useful hints to realize area-selective or position-controlled growth of carbon nanowalls.

Figure 6 shows an SEM image of carbon nanowalls grown on the patterned Ti film. The patterned Ti film was deposited on the Si substrate through a shadow mask by KrF excimer laser ablation using Ti target. The thickness of Ti film was approximately 10 nm. Carbon nanowalls were grown on the Si substrate that was partly covered with Ti film, by inductively coupled plasma-enhanced CVD employing $CH_4/H_2/Ar$ mixture for 30 min. As shown in Fig. 6, carbon nanowall growth was enhanced on the Ti film, compared with the carbon nanowalls grown on the Si surface. The height of the carbon nanowalls grown on the Ti film was 1.6 times greater

than that on the Si surface. It is considered that the nucleation rate of carbon nanowalls would depend on the class and forms of substrate materials, although the enhancement mechanism is unclear at present. Similar enhancement was observed on the thin layer or nanoparticles of Co, Pt, and Fe.

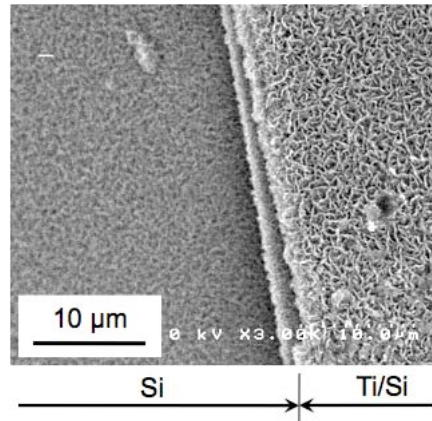


Fig. 6 SEM image of carbon nanowalls grown on the patterned Ti film by inductively coupled plasma-enhanced CVD employing $\text{CH}_4/\text{H}_2/\text{Ar}$ mixture for 30 min. The Ti film of about 10 nm thick was deposited area-selectively on the Si substrate by KrF excimer laser ablation using Ti target.

As described before, ion irradiation is considered to be one of important factors for the nucleation of carbon nanowalls. Therefore, we can expect that trenches are effective to separate the areas of carbon nanowall film. Since the flux of ions reaching the bottom surface of narrow or deep trenches would be reduced compared with that of ions irradiating the original surface, the nucleation of carbon nanowalls at the bottom of trenches would be inhibited.

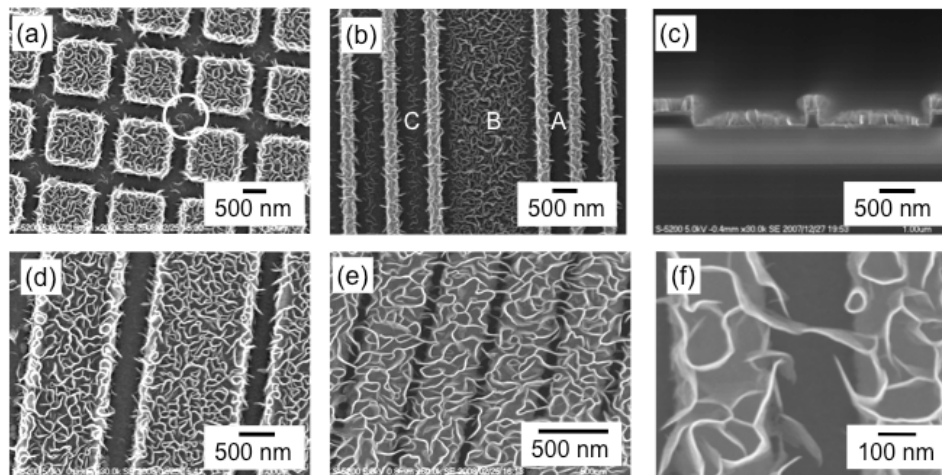


Fig. 7 SEM images of carbon nanowalls grown area-selectively on the patterned Ti film with trenches differing in width

Figures 7(a)–7(f) show SEM images of carbon nanowalls grown on the patterned Ti substrate. Ti film was deposited by the sputtering method on the patterned SiO_2 with trenches differing in width, and the thickness of the Ti film was approximately 50 nm. Carbon nanowalls were grown on the Ti film with trenches by electron-beam-excited plasma-enhanced CVD

employing CH_4/H_2 mixture. As shown in Fig. 7(a), carbon nanowalls were grown selectively on the Ti square regions, while the carbon nanowalls were slightly grown at the intersections of trenches indicated by an open circle. In this case, the trench width was approximately 300 nm. Figure 7(b) shows an SEM image of carbon nanowalls grown on the Ti stripe pattern with various trench widths. Carbon nanowalls were not grown on the bottom of trenches with a width of 300 nm indicated by “A”. In contrast, carbon nanowalls were formed at the bottom of wider trenches [“B” and “C” in Fig. 7(b)]. Figure 7(c) shows a cross-sectional SEM image of carbon nanowalls grown on the Ti stripe pattern with wider trenches. The carbon nanowall growth was not inhibited on the bottom of wide trenches. As shown in Fig. 7(d), in the case of the trenches with widths of 300–400 nm, carbon nanowalls were not grown on the bottom of trenches, allowing the growth of carbon nanowalls in the selected areas. On the other hand, when the width of trenches decreased less than 100 nm, these trenches could no longer separate the growth area [Fig. 7(e)]. By controlling the trench width carefully around 200 nm, isolated carbon nanowall bridging a trench between two lines could be formed reproducibly, as shown in Fig. 7(f). This structure would be useful to evaluate the electrical property of single carbon nanowall sheet.

In this way, carbon nanowalls can be grown selectively on the substrate through using patterned catalyst or with the help of deep trenches. These findings will broaden the field of application using carbon nanowalls.

Findings of the research will be presented at the international conferences (7th International Conferences on Reactive Plasmas (Paris, October 2010), 3rd International Symposium on Advanced Plasma Science and its Applications for Nitrides and Nanomaterials (Nagoya, March 2011)). Findings obtained in this research will also be submitted for publication to Japanese Journal of Applied Physics.

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